ARL-TR-8196 ● OCT 2017

US Army Research Laboratory

ECON-KG: A Code for Computation of Electrical Conductivity Using Density Functional Theory

by DeCarlos E Taylor

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
October 2017	Technical Report	1 Oct 2016–30 Sep 2017

4. TITLE AND SUBTITLE
ECON-KG: A Code for Computation of Electrical Conductivity Using Density Functional Theory

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
DeCarlos E Taylor

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army Research Laboratory
ATTN: RDRL-WML-B
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-8196

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
In this report, an implementation of the Kubo-Greenwood formula for electrical conductivity, for use with the Quantum Espresso software package, is presented. Details of the implementation and instructions for execution are presented, and an example calculation of the frequency-dependent conductivity of liquid sodium is presented and compared to experimental results.

15. SUBJECT TERMS
electrical conductivity, density functional theory, transport, Kubo–Greenwood, ECON-KG

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			DeCarlos E Taylor
Unclassified	Unclassified	Unclassified	UU	22	19b. TELEPHONE NUMBER (Include area code) 410-306-0853

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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Acknowledgments

All computations were performed at the US Army Research Laboratory Department of Defense Supercomputing Resource Center. I thank Dr Lázaro Calderin of the University of Florida for many fruitful discussions and for providing his KGEC software package for beta testing and validation.

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1. Introduction

The electrical conductivity of materials is of fundamental interest in a number of research areas, many of which are relevant to current US Army Research Laboratory (ARL) programs. In the Director's Strategic Initiative (DSI) "Transport in Complex Crystalline Materials Based on van der Waals Heterostructures", heterogeneous vdW solids are being fabricated experimentally as possible next-generation materials for electronic devices.[1] Knowledge of the *vertical* charge transport occurring *between* layers is critical as it may lead to design and fabrication of devices that are more tunable.

In another ARL application, the electrical conductivity of the boron carbide armor ceramic, one of the focus materials for the Materials in Extreme Dynamic Environments Collaborative Research Alliance, has been shown to be a function of pressure and carbon content.[2] Similarly, the electrical conductivity of explosive product gases has been shown to depend on carbon content,[3] and electrical conductivity models have become a requirement for input into continuum-level simulations being executed by researchers in the Multi-Threat Armor Branch. Although the increased electrical conductivity observed in detonation products of condensed explosives has received considerable attention experimentally,[4,5] conductivity values corresponding to regular intervals of temperature and pressure are required for accurate interpolation in continuum simulations.

In the absence of experimental data, particularly in the case of notional materials that have not yet been synthesized (such as the vdW heterostructures being explored in the aforementioned DSI), the electrical conductivity of materials can be obtained using first-principles quantum mechanical techniques. One approach for computing the conductivity from first principles is based on Boltzmann transport[6] theory where the electrical conductivity (σ) is proportional to the band velocities ν and lifetime τ:

$$\sigma_{\alpha\beta} \approx \tau * v_{\alpha}(k) * v_{\beta}(k) \,, \tag{1}$$

where α,β denote Cartesian direction. The band velocities in Eq. 1 are obtained by differentiating the band energies ε with respect to k points in the Brillouin zone—for example, $v \approx \frac{\partial \varepsilon}{\partial k}$. In practice, the differentiation is done numerically using a very dense grid of k-points as implemented in codes such as BoltzTrap.[7] The lifetime τ is a parameter and can be approximated by fitting to experimental data, which is mildly perplexing for materials where experimental data do not exist.

Another approach for computing conductivity is based on the Kubo-Greenwood (KG) formalism.[8] In this approach, the frequency (ω)-dependent electrical conductivity is computed as a weighted sum over k-points:

$$\sigma(\omega) = \sum_k \sigma_k(\omega) * W(k)\,, \tag{2}$$

where $W(k)$ is the weighting at integration point k. $\sigma_k(\omega)$ given by

$$\sigma_k(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{i,j=1}^{n}\sum_{\alpha=1}^{3}\left[F(\varepsilon_{i,k}) - F(\varepsilon_{j,k})\right] \times \left|\langle\Psi_{j,k}|\nabla_\alpha|\Psi_{i,k}\rangle\right|^2 \delta(\varepsilon_{j,k} - \varepsilon_{i,k} - \hbar\omega) \tag{3}$$

where m is the electron mass, Ω is the unit cell volume, F is the occupation number for bands i and j, ε is the band energy, and the index α denotes Cartesian direction for the momentum operator. The KG approach has the advantage that it does not require an estimate of the lifetime or numerical differentiation of band energies, and all requisite quantities can be obtained using quantum mechanical methods without fitting to experiment.

In this report, a Fortran 90 implementation of the KG formula, for use with the Quantum Espresso[9] software package, is presented. The program, called ECON-KG, is currently available at the ARL Defense Supercomputing Resource Center but can be easily ported to other Department of Defense computing facilities. Following details of the implementation and instructions for execution, the frequency-dependent conductivity of liquid sodium is presented and compared to experimental results.

2. Computational Methods

2.1 Implementation

The band energies, occupation numbers, and momentum matrix elements required in Eq. 3 are evaluated using the Quantum Espresso solid-state density functional theory software package. However, the public release version of Quantum Espresso only provides momentum elements where bands i and j of Eq. 3 lie in the valence and conduction bands, respectively. Unfortunately, this restriction is only applicable for calculations with integer occupation numbers and for calculations that use smearing (Fermi-Dirac, Gaussian, etc.) where there are non-integer occupations for bands near the Fermi level; matrix elements where indices i and j both lie in the valence band also contribute to the conductivity. Therefore, the Quantum Espresso source code was modified so that momentum matrix elements between *all* bands are now computed and written to disk along with the occupation numbers, band energies, and k-weights required to evaluate the conductivity.

In ECON-KG, the delta function appearing in Eq. 3 is broadened using a Gaussian function:

$$\delta\left(\varepsilon_{j,k} - \varepsilon_{i,k} - \hbar\omega\right) \rightarrow \frac{1}{\Delta\sqrt{\pi}} e^{-\frac{\left(\varepsilon_{j,k}-\varepsilon_{i,k}-\hbar\omega\right)^2}{\Delta^2}}, \qquad (4)$$

where the broadening factor Δ is an input parameter set by the user. This parameter can have significant effects on the computed conductivity as has been extensively discussed by Knyazev and Levashov,[10] who tested the sensitivity of results for aluminum using broadening factors ranging from 0.02 to 0.2 eV. Pozzo et al.[11] suggest a factor that is equal to the average spacing between the computed eigenvalues and used values ranging from 0.0012 to 0.045 eV for their work on sodium. In both cases, the convergence of the conductivity with respect to the broadening factor was improved by increasing the system size, and all of these variables have to be considered when converging values of the conductivity.

2.2 Execution

In order to compute the conductivity using ECON-KG, the following 3 steps are necessary:

1) Perform a single-point self-consistent field (SCF) calculation to get a set of valence and conduction bands for the system using the "pw.x" executable from the Quantum Espresso suite.

2) Using the converged bands, compute the momentum matrix elements using the *locally modified* (as described previously) "bands.x" executable from the Quantum Espresso suite.

3) Run the ECON-KG executable.

Sample Quantum Espresso input files (for steps 1 and 2) using liquid sodium as an example are given in the Appendix.

Given a set of bands and momentum matrix elements, the ECON-KG executable is then run to compute the conductivity. The ECON-KG input file ("kg.input") is simply a list of user-defined variables formatted as follows:

```
13117.18      ! Volume in Bohr
0.05          ! Delta function factor (eV)
486           ! Number of Electrons in System
1.73          ! Fermi Energy (eV)
5.0           ! Fermi Window (eV)
0.001 2.0 0.002    ! Frequency Range
```

Specifically, line 1 is the unit cell volume in atomic units, line 2 is the Gaussian broadening factor for Eq. 4 in eV, line 3 is the number of electrons for the system, and line 4 is the Fermi energy (in electronvolts) obtained from the SCF calculation. Line 5, the "Fermi Window", sets the range of band energies (measured from the Fermi level) that are included in the calculation. In the input above, all bands within 5.0 eV of the Fermi level are included. As shown in Eq. 3, the conductivity is frequency dependent, and ECON-KG will provide conductivity values for all frequencies within a range specified by the user. The frequency range is defined on line 6, in units of electronvolts, where the first and second numbers are the lower and upper frequency limits, respectively, and the third number is the spacing between points within those bounds. In the example above, ECON-KG will compute the conductivity for values from 0.001 to 2.0 eV with a spacing of 0.002 eV between successive points. The conductivity corresponding to zero frequency ("DC" conductivity) cannot be directly computed using the KG expression since $\omega = 0$ introduces a singularity. Therefore, the DC conductivity must be obtained by extrapolation of the low-frequency values to zero.

2.3 Output

The ECON-KG output consists of a single table where each row contains conductivity values for each frequency requested by the user. Each row of the 6-column table contains the following data:

Frequency(eV) Conductivity(S/m) σ_{xx}(S/m) σ_{xx}(S/m) σ_{zz}(S/m) Sum_Rule

where column 1 is the frequency, column 2 is the trace of the conductivity tensor (Siemens/meter), and columns 3, 4, and 5 are the diagonal components of the conductivity tensor that contribute to the trace. The last column, "Sum_Rule", reports the value of the following integral:

$$\frac{2m\Omega}{\pi e^2 N}\int_0^\infty \sigma(\omega)d(\omega)\ , \tag{5}$$

where N is the number of electrons in the system. This integral, approximated using the trapezoid rule in ECON-KG, should equal 1 (though in practice it is generally <1) and serves as a check on the quality of the calculation.

3. Example

As an example application, the conductivity of liquid sodium has been computed using the sample inputs given in the Appendix. The input structure was extracted from a molecular dynamics simulation of liquid sodium, at a temperature of 950 K, using the Perdew–Burke–Ernzerhof[12] density functional with Fermi–Dirac

smearing and an electronic temperature of 0.082 eV. A plot of the optical conductivity, as a function of k-point sampling for this structure, is shown in Fig. 1. The plot contains curves for multiple k-point grids ranging from the Gamma point up to 8 × 8 × 8 Monkhorst–Pack[13] meshes. The experimental zero frequency value (2.26×10^6 S/m) shown in the figure (red star) was obtained by extrapolation of measurements reported by Freedman and Robertson[14] to 950 K. As shown, convergence with respect to k is slow, particularly in the low-frequency regime.

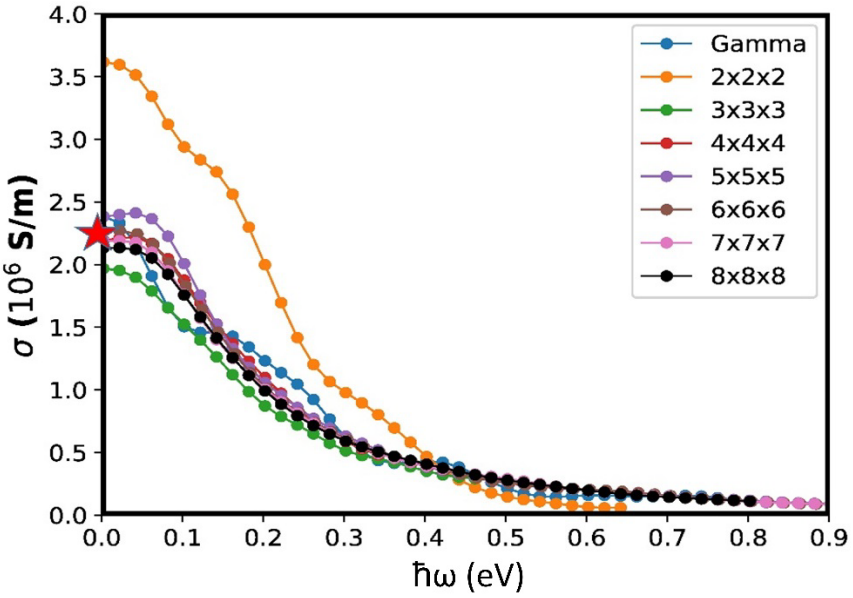

Fig. 1 Optical conductivity of liquid sodium using multiple k-point grids. Experimental value (red star) taken from Freedman and Robertson[14].

The predicted DC conductivities, obtained by linear extrapolation, are given in Table 1, and a plot of these values versus k-point grid size is given in Fig. 2. The extrapolations were performed with the SciPy Python library using conductivity values from 0.007 to 0.15 eV for each curve.

Table 1 DC conductivity (10^6 S/m) for each k-point grid

k-Mesh	σ(ω=0)
Gamma	2.43
2 × 2 × 2	3.78
3 × 3 × 3	2.12
4 × 4 × 4	2.46
5 × 5 × 5	2.72
6 × 6 × 6	2.52
7 × 7 × 7	2.45
8 × 8 × 8	2.37
Experiment	**2.26**

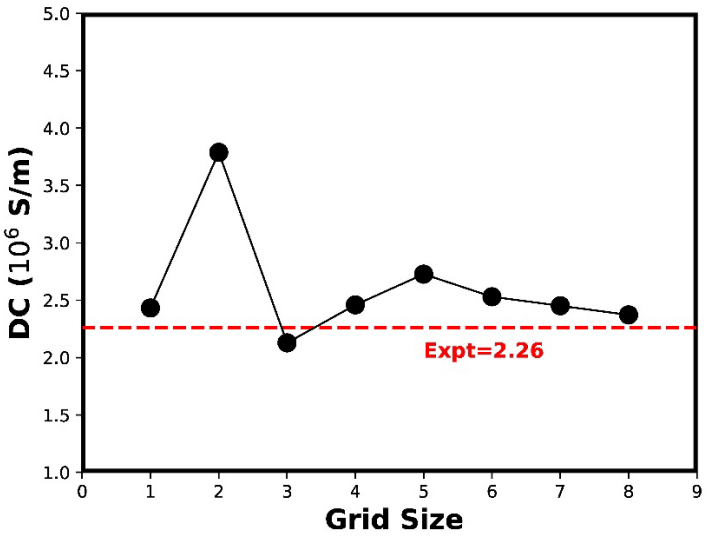

Fig. 2 DC conductivity of liquid sodium as a function of k-point grid size

As shown in Table 1, the results are in fair agreement with the experiment. However, the error as a function of k is oscillatory, and with a mesh size of 6 × 6 × 6, the results are only starting to show convergence (see Fig. 2).

4. Conclusion

The example results presented in this work were obtained using a single structure extracted from a molecular dynamics trajectory. In practice, one should use multiple structures, with appropriate averaging, to determine the conductivity values. However, for brevity's sake, only a single structure was used for the example application presented in the report. The results in this work are in fairly good agreement with the experiment. However, in the author's experience, the level of agreement can shift dramatically (factor of 10 or more) depending on density functional, system size, and input parameters to ECON-KG. The results can be very sensitive to the number of bands and delta function width, and convergence with respect to these quantities can be challenging.

Finally, I should acknowledge Dr Lazaro Calderin of the University of Florida who I discovered, during development of ECON-KG, was also developing an implementation of the KG formalism in conjunction with Quantum Espresso. I thank Dr Calderin for many fruitful discussions and for the opportunity to be a beta tester of his program[15], which was used to debug and validate the results obtained with ECON-KG.

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Appendix. Sample Input files

The following is a sample Quantum Espresso input file for computing a converged set of bands for liquid sodium using the pw.x executable from the Quantum Espresso suite. Keyword descriptions and input syntax are available in the Quantum Espresso user manual.

```
 &CONTROL
   calculation = "scf",
   pseudo_dir  = "/usr/people/detaylor/PSEUDOPOTENTIALS/ultra",
   prefix      = "dtpoly",
   nstep = 1
  wf_collect = .true.
 /
 &SYSTEM
   ibrav       = 0,
   nat         = 54,
   ntyp        = 1,
   ecutwfc     = 30.D0,
   vdw_corr = "grimme-d2"
   nbnd=280
   occupations = "smearing"
   smearing = "fd"
   degauss = 0.006
 /
 &ELECTRONS
   electron_maxstep = 500,
   conv_thr    = 1.D-6,
   mixing_beta = 0.3D0,
   scf_must_converge = .false.
 /
 &IONS
 /
 &CELL
 /
 CELL_PARAMETERS angstrom
  12.480 0 0
  0 12.480 0
  0 0 12.480
 ATOMIC_SPECIES
 Na  1.00  na.upf
 ATOMIC_POSITIONS {angstrom}
 Na    -6.49145  -5.56509   7.46734
 Na    -2.63957   9.48177   0.83205
 Na     9.14960  -1.19936  -0.61690
 Na    -2.88286  18.74158   5.66213
 Na   -13.51095  15.30019  13.18334
```

Na	12.53685	-3.57070	9.70781
Na	-9.29464	14.31882	-8.44320
Na	-12.00947	-4.46376	0.09270
Na	1.70977	3.09272	5.64892
Na	7.78536	0.94219	18.73531
Na	-3.50624	-7.49415	16.25346
Na	2.02219	-2.22495	4.69396
Na	-6.14664	7.98090	4.55669
Na	-0.81211	18.41742	-15.53245
Na	-2.75103	15.48755	-0.72738
Na	4.25365	7.57677	12.72076
Na	15.75801	14.17200	-1.23555
Na	7.68093	15.46983	20.90631
Na	7.20992	9.10673	13.03992
Na	18.22595	0.77448	-3.65508
Na	11.58326	-0.24269	10.80184
Na	-2.48933	-11.93361	8.67884
Na	1.99670	-13.11942	14.66121
Na	2.35281	-1.45250	11.17339
Na	-2.25883	3.15010	4.63930
Na	4.85383	5.35284	-2.36860
Na	12.83331	5.24590	3.13106
Na	7.02326	4.79217	-1.14337
Na	4.00584	0.78262	18.36582
Na	12.50268	12.51815	4.52492
Na	5.78203	-2.72011	-5.59039
Na	-4.00686	6.59546	1.39452
Na	12.01031	11.46302	1.91613
Na	6.74905	3.14472	4.42347
Na	2.44556	19.70637	20.04626
Na	17.92583	15.63488	7.49345
Na	-1.56790	-2.23829	7.54851
Na	5.69915	13.74492	2.27491
Na	12.09839	-3.83016	5.82794
Na	10.72698	4.07149	8.18170
Na	7.94006	0.98534	10.44330
Na	19.90926	-3.95616	10.43586
Na	0.01664	7.96829	-9.70577
Na	3.30370	8.37723	9.82259
Na	14.48450	5.28234	-1.30440
Na	21.55710	10.20285	-7.61440
Na	13.51033	4.36419	-3.36310
Na	4.09043	17.01501	1.34137
Na	2.62843	7.74397	4.58241
Na	26.78942	0.63389	8.15922
Na	5.67407	-1.12595	-0.10256

```
Na     6.28368  10.45636  15.06059
Na     4.32227  10.90205   9.00709
Na     3.73724   4.93973   4.76614
K_POINTS {automatic}
2 2 2 0 0 0
```

Below is a sample Quantum Espresso input file for computing momentum matrix elements using the modified bands.x executable. Keyword descriptions and input syntax are available in the Quantum Espresso user manual.

```
&BANDS
 prefix      = "dtpoly"
 outdir = "/p/work1/detaylor/pw2gw/today/conduct/sodium-liquid"
 filband= "bands.dat"
 lp = .true.
 filp = "carlos.mom"
```

List of Symbols, Acronyms, and Abbreviations

ARL	US Army Research Laboratory
DC	direct current
DSI	Director's Strategic Initiative
eV	electronvolt
KG	Kubo-Greenwood
SCF	self-consistent field

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